ELECTROCHEMICAL ELEMENT FOR USE AT HIGH TEMPERATURES

BACKGROUND OF THE INVENTION

This invention relates to an electrochemical element for use at high temperatures.
Electrochemical elements comprise a cathode and an anode, and an electrolyte which is arranged between the cathode and the anode. The cathode and anode generally comprise metallic current collectors and an active material, which can be the current collector material itself. An electrochemical cell that produces electricity as a result of a spontaneous chemical reaction is called a galvanic cell. An electrochemical element or cell in which a non-spontaneous chemical reaction is driven by an external current source is called an electrolytic cell.

An electrolyte is a compound, or combination of compounds, capable of conducting electricity in the form of an ionic current, carried by mobile ions. Examples of an electrolyte are a salt, or a mixture of salts, in its solid or molten state or dissociated into its ions in a solvent in which the solvent is not or only slightly dissociated.

Electrochemical elements may be configured as a primary battery or a rechargeable battery or an electrochemical capacitor. Rechargeable batteries are often referred to as secondary batteries and non-rechargeable batteries are often referred to as primary batteries.

A battery is a device that stores electrical energy using one or more electrochemical cells. The cells can be connected in series or parallel. The physical

construction of a cell is such that a direct reaction of
the chemicals stored in the electrodes is prohibited by
physically separating the electrodes by an electrolyte.
When the two electrodes are connected through an external
5   circuit, a galvanic cell will produce an electrical
current. Electrons will flow through the external
circuit, ions will flow through the electrolyte.

The reactions at the electrodes, involving transfer
of electrons from one substance to another and thus the
10   reduction and oxidation of the substances, are called
redox reactions. The electrode where oxidation takes
place is called the anode, the electrode where reduction
takes place is called the cathode.

A rechargeable battery is a battery or
15   electrochemical cell in which the chemical reaction,
producing the electrical current upon discharge, is
easily chemically reversible. A rechargeable battery can
be recharged by applying an electrical current to its
electrodes or terminals. Preferably, a rechargeable
20   battery can be recharged hundreds of times without
significant loss of storage capacity. A primary battery
can be discharged only once and has to be disposed off
afterwards.

The active material of the positive electrode in a
25   primary battery will be reduced in the discharge process
and is therefore also known as the cathode material. Vice
versa is material at the negative electrode known as the
anode material. The same naming convention is used for
the active materials of a rechargeable battery in its
30   charged state (a galvanic cell).

Batteries are widely used as a source of electrical
energy for a variety of applications. Rechargeable
batteries are used for many applications to avoid the

replacement and disposal of primary batteries. Moreover,
their use allows the remote operation of devices in
difficult to reach locations where exchange of primary
batteries is not practically possible but where

5   recharging a battery would be feasible. An example of
such a location is in a wellbore for oil and gas
production. Not only are downhole locations difficult to
reach, the environmental conditions are also harsh with
temperatures in the range of 60 to 200 °C which demands

10   an electrochemical element suitable for high
temperatures.

       Most batteries are configured for use in a specified
temperature range, which is typically capped due to
instability, disintegration, melting and/or evaporation

15   of the chemical compounds in the battery above a certain
temperature. A typical operating range for batteries is
between -40 and +60 °C.

       Many rechargeable battery chemistries have been
developed. Examples are Lead-acid, Nickel-Cadmium,

20   Nickel-metalhydride, and Lithium (Lithium-metal and
Lithium-ion) batteries. From these, batteries based on
Lithium chemistry are most interesting since they offer
the highest energy density because Lithium has the lowest
reduction potential known (-3.045 V versus a standard

25   hydrogen electrode) and has a high specific storage
capacity of 3828 mAh/g (for a Lithium 7 isotope=^{7}Li).
However, the formation of Lithium dendrites on the
Lithium anode in rechargeable batteries with electrolytes
based on organic solvents has been a safety concern. This

30   has led to the development of Lithium-ion batteries (Li-
ion) in which the Lithium anode has been replaced with an
intercalation material.

An intercalation or insertion compound is a host compound in which a guest species can be stored or from which it can be extracted. Examples of three dimensional intercalation materials are $LiMn_2O_4$ and $Li_4Ti_5O_{12}$ which

5   reversibly allow the extraction and/or insertion of Lithium ions as guest species from/in their cubic crystal lattice structures.

An intercalation-reaction or insertion-reaction is defined as a reaction, generally reversible, that

10   involves the introduction or removal of a guest species into or from a host structure without a major structural modification of the host. In the strictest sense, intercalation refers to the insertion of a guest into a two-dimensional host; however, the term also now commonly

15   refers to one-dimensional and three-dimensional host structures. An example is the insertion of Lithium into layered TiS_2: $x\,Li + TiS_2 \rightarrow Li_xTiS_2$ ($0 \leq x \leq 1$) (this example is described in the IUPAC Compendium of Chemical Terminology, 2nd Edition, 1997). Here, x is the variable

20   amount of Lithium intercalated in TiS_2. The given limits ($0 \leq x \leq 1$) indicate the compositional range over which x can be varied in a reversible way. Between these limits, Li_xTiS_2 exhibits a specific potential curve as function of x when measured versus a suitable reference electrode,

25   which is Lithium metal in case of Lithium intercalation. Many reversible intercalation materials are known, each having a specific potential curve associated with a specific reversible composition range ($x_{min} \leq x \leq x_{max}$). These potential curves can be characterised by a lower-

30   and an upper reversible-potential-limit (RPL_{low} and RPL_{upp}, respectively) and an average potential V_{avg}. Some examples are given in table 1.

Table 1. Intercalation materials with reversible composition range and associated capacity, RPL_{low}, average-potential, and RPL_{upp} versus Li/Li^+. Potentials for $Mg_xMo_3S_4$ are versus Mg/Mg^{2+}.

Material	($x_{min} \leq x \leq x_{max}$)	C (Ah/kg)	RPL_{low} (V)	V_{avg} (V)	RPL_{upp} (V)
$Li_{1+x}CrTiO_4$	$0 \leq x \leq 1$	157	1.0	1.5	2.0
$Li_{4+x}Ti_5O_{12}$	$0 \leq x \leq 3$	175	1.05	1.55	2.05
$Li_{4+x}Mn_5O_{12}$	$0 \leq x \leq 3$	161	2.4	2.9	3.3
Li_xTiS_2	$0 \leq x \leq 1$	240	1.5	2.1	2.5
$Li_{1+x}Ni_{0.5}Mn_{1.5}O_4$	$0 \leq x \leq 1$	146	2.5	2.9	3.3
$Li_{1+x}Mn_2O_4$	$0 \leq x \leq 1$	148	2.5	2.9	3.3
$Li_{1-x}FePO_4$	$0 \leq x \leq 1$	160	3.0	3.4	3.8
$Li_{1-x}Mn_2O_4$	$0 \leq x \leq 0.8$	120	3.5	4.1	4.2
$Mg_xMo_3S_4$	$0 \leq x \leq 1$	120	0.2	1.1	2.0

The potentials measured versus Mg/Mg^{2+} can easily be converted to potentials versus Li/Li^+ by using the known reduction potentials versus the standard hydrogen electrode (SHE): $Li^+ + e = Li$ -3.045 V and $Mg^{2+} + 2e = Mg$ -2.375 V. This means that the upper cut-off potential of $Mg_xMo_3S_4$ of 2.0 V versus Mg/Mg^{2+} becomes 2.67 V versus Li/Li^+.

In the field of batteries, it is common to use so called lower- and upper cut-off potentials. These do not necessarily coincide with the RPL potentials of the active materials used. The cut-off potentials are a means of controlling the composition of the intercalation material in a battery and determine the utilisation of

the storage capacity. Setting the cut-off potentials to a
window wider than the window defined by the RPL values
may result in the irreversible oxidation or reduction of
the active materials and/or the electrolyte, leading
ultimately to failure of the battery. Setting the cut-off
potentials to a window smaller than the RPL window
results in a lower utilisation of the storage capacity of
the active materials, but in general leads to a longer
battery life. The current state-of-the-art Lithium and
Li-ion batteries comprise positive electrode (cathode)
materials like MnO_2, $LiCoO_2$, $LiNi_{0.8}Co_{0.2}O_2$, and $LiMn_2O_4$.
Carbonaceous materials like graphite, MCMB, and petroleum
coke are used as negative (anode) materials in Li-ion
batteries. Batteries made by a combination of such
cathode and anode materials show attractive high voltages
between 3 and 4 V.

The electrolytes used in these batteries are based on
Lithium salts as for example $LiPF_6$, $LiBF_4$, $LiClO_4$, and
$LiAsF_6$ dissolved in (mixtures of) organic solvents like
for example ethylene-carbonate (EC), di-methyl-carbonate
(DMC), propylene-carbonate (PC), ethyl-methyl-carbonate
(EMC) etc. These solvents are flammable and show
considerable vapour pressures at temperatures above
60 °C. Furthermore, these electrolytes can strongly react
with the other battery components if the battery
temperature rises above 60 °C, for example in the case of
over-charging or internal shorting, imposing a potential
danger. The operating temperature range is therefore
limited from about -40 °C to +80 °C, which is similar to
that found for the aqueous electrolytes.

Rechargeable battery chemistries that are able to
operate at higher temperatures can be found in the molten

salt systems, for example the system Li//FeS$_2$ which, depending on the composition of the electrolyte, operates between 350 and 550 °C, or the system Na//S which operates between 220 and 350 °C. Therefore, there is a gap in the operating temperature range of current rechargeable battery technology between about 80 and 220 °C. The reason for this gap lies in the inadequate thermal properties of the available electrolytes.

The current technology of primary batteries, however, does not show such a temperature gap. The system Li//SO$_2$Cl operates between −40 and +150 °C or, by alloying Lithium with Magnesium, between 70 to 200 °C. In this battery chemistry the electrolyte is the in-situ reaction product when Lithium metal contacts SO$_2$Cl.

International patent application WO 01/15258 (D.R. MacFarlane et al.) discloses a solid-state conductive material comprising a pyrrolidinium or other cation. It further discloses that an anode of a Lithium battery may comprise a Lithium intercalation material.

Recent advances in the research of so called ionic liquids have shown that these materials have very promising properties to be used for a new generation of battery electrolytes, especially for high temperature batteries. Ionic liquids are known and have gained a lot of attention for their suitability in green chemistry. In contrast to the organic solvents, ionic liquids are non-flammable, non-volatile, and are chemically stable over a wide temperature range, up to 400 °C. Furthermore, they can be mixed with a wide range of electrolyte salts, allowing very high electrolyte salt concentrations. The conductivities of these electrolytes is comparable or sometimes higher than comparable organic solvent based

systems. Many of the ionic liquids are in their liquid
state in a wide temperature range, starting below room
temperature and ranging up to about 400 °C.

An article by D.R. MacFarlane, *et al.*, (Journal of
Phys. Chem. B, 103 (20) 1999, 4164) discloses that, among
the known ionic liquids, some members of the
pyrrolidinium family of ionic liquids show the widest
electrochemical stability windows of up to 5.5 V,
measured between glassy-carbon electrodes at 25 °C. The
electrolyte stability window is the potential range,
bounded by an oxidation- and a reduction-potential, in
which the electrolyte is not oxidised nor reduced.

It is known for organic-solvent based electrolytes
that a wider stability window is found when inert
electrodes are used, like glassy-carbon or Platinum, than
when electrodes containing active materials are used,
like intercalation compounds. In that case, smaller
electrolyte stability windows are found due to
interaction of the electrolyte with the active materials.
Furthermore, increasing the temperature enhances these
interactions, resulting in an even smaller stability
window. The large stability window of the pyrrolidinium
based ionic liquids renders them as especially
interesting for the application in electrolytes for use
at high temperatures.

It is known that ionic liquids may be used as an
electrolyte in electrochemical elements if an electrolyte
salt (e.g. a Lithium salt) is added to the ionic liquid
in order to obtain ionic conductivity of the required
ion. The term ionic liquid is not well defined in
literature but refers in general to a molten salt or to a
liquid which consists of fully or almost fully
dissociated ions. Room temperature ionic liquids are thus

ionic liquids that are in the liquid state at room temperature. 'Room temperature' is often defined as a temperature close to 25 °C but can be as high as 80 °C. It has to be noted therefore that not all compounds classified as 'ionic liquids' in the open literature have a melting point below 80 °C.

In this specification and claims ionic liquids are defined as 'ionic compounds', which are liquid in the operating temperature range. An ionic liquid may comprise a liquid mixture of ionic compounds.

It is known that in electrochemical elements that are configured for use at temperatures below 60 °C the electrolyte layer may comprise an extensive range of materials with ionic conductivity, such as electrolyte solutions comprising salts, which are dissociated into ions when dissolved in a solvent.

US patent 5,827,602 (Covalent Associates, Inc.) discloses the hydrophobic ionic liquids based on cations comprising pyridinium, pyridazinium, pyrimidinium, pyrazinium, imidazolium, pyrazolium, thiazolium, oxazolium, and triazolium. Also disclosed is the use of these ionic liquids in an electrochemical cell or a capacitor. No evidence of a stable functioning rechargeable battery incorporating these ionic liquids is shown and no operating temperature range is claimed.

US patent 5,965,054 (Covalent Associates, Inc.) discloses the use of the hydrophobic ionic liquids based on cations comprising pyridinium, pyridazinium, pyrimidinium, pyrazinium, imidazolium, pyrazolium, thiazolium, oxazolium, and triazolium in an electrolyte with a salt dissolved in a polar organic liquid or dissolved in liquid sulfur dioxide. The use of a polar solvent renders the known electrolyte not suitable for

high temperature applications due to vapour formation. No evidence of a stable functioning rechargeable battery incorporating these ionic liquids is shown and no operating temperature range is claimed.

5   US patent 6,326,104 (Electrochemical Systems, Inc.) discloses the use of electrolytes based on ionic liquids comprising the pyrazolium cation. This prior art reference provides four examples related to Lithium rechargeable batteries (a $LiMn_2O_4$ cathode and a Lithium

10   metal anode), wherein one cell was tested at 55 °C and three cells were tested at room temperature. All cells showed lower then expected capacities and/or fading, i.e. only an indication is given of the potential use. Also, a description was given that the following ionic liquids

15   were not stable against metallic Lithium: 1-ethyl-3-methyl-imidazolium-tetrafluoroborate and 1,2-dimethyl-3-propylimidazolium-tetrafluoroborate.

US patent 5,855,809 (Arizona Board of Regents) discloses the use of electrolytes based on the following

20   ionic liquids: X_3PNPOX_2, X_3PNCH_3, X_3PNSO_2X, XSO_2CH_3, CH_3COX, and $CH_3CH_2NPX_3$ where X is a halogen atom. The results of one battery test are shown for a cell comprising a $LiMn_2O_4$ cathode and a Lithium metal anode with $0.3LiAlCl_4$ in $0.7(AlCl_4{}^-/SO_2NPCl_3{}^+)$ as the

25   electrolyte. However, FIG 16 in this patent is not showing the known voltage profile as function of x for a cell with a $Li_xMn_2O_4$ (0≤x≤1) cathode and a Lithium metal anode. Moreover, the charge capacity is twice the discharge capacity which means that the efficiency is

30   poor. It was further indicated that this cell behaviour was reversible over 50 cycles.

US patent 6,552,843 (Innovative Technology Licensing LLC) discloses a reversible electrodeposition device for controlling the propagation of electromagnetic radiation comprising an electrolyte based on ionic liquids
5   comprising a cation based on *N*-methyl-pyrrolidinium, pyrrolidinium, 1-ethyl-3-methyl-imidazolium, 1-*N*-butyl-pyridinium, 2-methyl-1-pyrrolinium or 1-ethyl-imidazolium. A reversible electrodeposition device is an electrochemical device that can only operate as an
10   electrolytic cell. Furthermore, the electrodes do not contain intercalation materials.

International patent application WO 02/063073 (B.R. Mattes, W. Lu) discloses the use of ionic liquids in electrochemical devices with conjugated polymers as
15   the active materials in the electrodes. The cation of the ionic liquid is based on pyridinium, pyridazinium, pyrimidinium, pyrazinium, imidazolium, pyrazolium, thiazolium, oxazolium, triazolium, ammonium, pyrrolidinium, pyrrolinium, pyrrolium, and piperidinium.
20   Conjugated polymers are polymer materials with alternating single and double bonds along the polymer chain. No battery related data are disclosed in this prior art reference.

Electrochemical elements for use at a temperature
25   above +60 °C are known from International patent applications WO 0180344 and WO 0209215. The known electrochemical elements comprise a granular electrolyte layer, which is substantially free of polymer binder materials that would evaporate at an elevated
30   temperature. A disadvantage of the use of a granular electrolyte layer is that the physical contact surfaces between the granules are relatively small, which results in a limited transfer of ions via the granules between

the cathode and anode, and in a moderate electric power output of the element. The batteries known from these prior art references are suitable for use at a temperature up to about 100 °C and have a limited output

5   of electric power, which is expected to be a result of the limited contact areas between the solid state particles in the electrolyte.

International patent application WO2004/082059 discloses various pyrrolidinium based room temperature

10   ionic liquids for use in energy storage devices, such as secondary lithium batteries.

The referenced prior art shows that ionic liquids can be used to make electrolytes.

Applicant now has discovered that only certain

15   combinations of active materials and electrolytes comprising a pyrrolidinium based ionic liquid result in reversibly operating rechargeable batteries, especially at temperatures between 60 and 150 °C.

It is an object to provide an electrochemical element

20   which is suitable for use at a high temperature.

It is a further object of the present invention to provide an electrochemical element which is suitable for use as a rechargeable battery, which can be used as an efficient energy source at a temperature above 50 °C, in

25   particular in the range from 60 to 150 °C.

It is a further object of the present invention to provide a method for generating electrical energy by means of a rechargeable battery in an underground wellbore, such as an oil or gas production well, in which

30   the temperature may be between 60 and 200 °C or a geothermal well in which the temperature may be up to several hundred degrees Celsius.

SUMMARY OF THE INVENTION

The electrochemical element according to the invention comprises a cathode, an anode and an electrolyte arranged between the cathode and anode, which electrolyte comprises an ionic liquid comprising an anion and a cation, which cation comprises a pyrrolidinium ring structure; and wherein the active material of the cathode comprises an intercalation material having an upper reversible-potential-limit of at most 4 V versus Li/Li^+.

Applicant has discovered that intercalation materials with an upper reversible-potential-limit of more than 4 V versus Li/Li+ are not suitable for reversible use. It is believed that the interaction between the electrolyte and these materials cause degradation of the materials and/or electrolyte resulting in loss of capacity, especially when used at temperatures above 70 °C.

Suitable intercalation materials with an upper reversible-potential-limit of at most 4 V are for example: $LiFePO_4$, $Li_3Fe_2(PO_4)_3$, $Li_4Mn_5O_{12}$, $Li_2Mn_4O_9$, MnO_2, FeS_2, LiV_3O_8, V_2O_5, TiS_2, TiO_2, $Li_2Ti_3O_7$, $LiTi_2(PO_4)_3$, $NaTi_2(PO_4)_3$, TiP_2O_7, LiV_2O_4, $Li_4Ti_5O_{12}$, $LiCrTiO_4$, $LiTi_2O_4$, CuO, $MgMo_3O_4$, Li_3FeN_2, Li_7MnN_4. Particularly suitable intercalation materials are $LiFePO_4$, $Li_4Mn_5O_{12}$, TiS_2, $Li_4Ti_5O_{12}$ and $LiCrTiO_4$.

It is observed that WO 01/15258 discloses a solid-state conductive material comprising a pyrrolidinium or other cation. It further discloses that an anode of a Lithium battery may comprise a Lithium intercalation material.

It is believed that a solid-state conductive material has a lower ionic conductivity than an ionic liquid. The use of an ionic liquid in the electrochemical element

according to the present invention instead of a solid-state conductive material will result in a higher power density and therefore in a better performance of the electrochemical element.

When used in this specification and claims an active intercalation material is defined as an intercalation material that takes part in the redox reaction in the electrodes.

As an alternative to the use of an active intercalation material the anode of an electrochemical element may comprise a conjugated polymer. International patent application WO/02/063073 discloses an electrochemical element with an anode or cathode comprising a conjugated polymer as the major constituent of the active material.

The electrochemical element according to the invention may be configured for use as a primary or a rechargeable battery or an electrochemical capacitor at high temperature, such as a temperature above 50 °C and particularly at a temperature between 60 and 150 °C.
It is furthermore preferred that the pyrrolidinium ring structure has the formula: N-R_1-N-R_2-pyrrolidinium, wherein R_1 and R_2 are alkyl groups and that R_1 is methyl and R_2 is butyl or hexyl.

The anion of the ionic liquid preferably comprises any of the following compounds:

- ClO_4^-, AsF_6^-, PF_6^-, BF_4^-, a halogen ion, $N(CF_3)_2^-$, $N(CF_3SO_2)_2^-$ ('TFSI'), $CF_3SO_3^-$, and $N(CH_3SO_2)_2^-$, $N(C_2F_5SO_2)_2^-$, $B(C_2O_4)_2^-$, $C(CF_3SO_2)_3^-$.

It is also preferred that the alkali salt comprises a Lithium salt which may comprise any of the following compounds:

- $LiN(CF_3SO_2)_2$ ('LiTFSI'), $LiCF_3SO_3$, $LiClO_4$, $LiBF_4$, $LiPF_6$, and $LiAsF_6$, $LiB(C_2O_4)_2$, $LiC(CF_3SO_2)_3$.

Alternatively the salt may comprise $MgCF_3SO_2$ or $Mg(ClO_4)_2$.

The cathode suitably comprises $Li_4Ti_5O_{12}$, $Li_{4-y}Mg_yTi_5O_{12}$ ($0 \leq y \leq 1$), $LiCrTiO_4$, V_2O_5, TiS_2, $Li_4Mn_5O_{12}$, $Li_{4-y}Mg_yMn_5O_{12}$ ($0 \leq y \leq 1$) or $Li_{1-y}M_yFePO_4$, where M=Mg, Nb, Zr, Ti or Al ($0 \leq y \leq 0.02$), as the active material and as the major constituent by mass.

The anode suitably comprises Lithium, $Li_4Ti_5O_{12}$, $Li_{4-y}Mg_yTi_5O_{12}$ ($0 \leq y \leq 1$), $LiCrTiO_4$, as the active material.

The invention also provides a method of providing electrical energy in an underground wellbore, wherein the energy is provided by an electrochemical element according to the invention. The underground wellbore may form part of an oil and/or gas production well or a geothermal well.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be described in more detail with reference to the accompanying drawings wherein:

FIG. 1 A,B and C depict three examples of pyrrolidinium cations comprising a ring structure of four Carbon atoms and one Nitrogen atom;

FIG. 2 is a graph showing charge and discharge capacity of the cell with a $Li_4Ti_5O_{12}$ cathode and a Lithium metal anode 110 °C with LiTFSI in P_{14}TFSI in the molar ration 0.38:0.62. The capacity is given as

percentage of the expected sample capacity based on the active mass and theoretical capacity;

FIG. 3 is a graph showing voltage curves for cycle number 7, 107 and 207 of the cell with a $Li_4Ti_5O_{12}$ cathode and a Lithium metal anode 110 °C with LiTFSI in $P_{14}TFSI$ in the molar ration 0.38:0.62;

FIG. 4 is a graph showing charge and discharge capacity of the cell with a $Li_4Ti_5O_{12}$ cathode and a Lithium metal anode 110 °C with 2.0 mol/kg LiTFSI in $P_{16}TFSI$. The capacity is given as percentage of the expected sample capacity based on the active mass and theoretical capacity;

FIG. 5 is a graph showing charge and discharge capacity of the cell with a TiS_2 cathode and a Lithium metal anode 110 °C with LiTFSI in $P_{14}TFSI$ in the molar ration 0.40:0.60. The capacity is given as percentage of the expected sample capacity based on the active mass and theoretical capacity;

FIG. 6 is a graph showing voltage curve for cycle 50 of the cell with a TiS_2 cathode and a Lithium metal anode 110 °C with LiTFSI in $P_{14}TFSI$ in the molar ration 0.40:0.60;

FIG. 7 is a graph showing charge and discharge capacity of the cell with a $Li_4Ti_5O_{12}$ cathode and a Lithium metal anode 150 °C with LiTFSI in $P_{44}TFSI$ in the molar ration 0.30:0.70. The capacity is given as percentage of the expected sample capacity based on the active mass and theoretical capacity;

FIG. 8 is a graph showing the potential curves of three cells with a $LiMn_2O_4$ cathode and a Lithium metal anode. Cell A contains a reference electrolyte based on

organic solvents at 25 °C and shows the expected
characteristic potential curve. Cells B and C contain
pyrrolidinium based electrolytes at 110 °C and show
failure of the cells starting; and

FIG. 9 shows the characteristic flat potential curve
for $LiFePO_4$ cathode and a Lithium metal anode 110 °C with
LiTFSI in P_{14}TFSI in the molar ration 0.40:0.60. The
potential is given as function of time.

DETAILED DESCRIPTION OF THE INVENTION

FIG.1A depicts that a pyrrolidinium compound
comprises a positively charged ring structure of four
carbon atoms and one nitrogen atom. The depicted compound
has the formula: $N-R_1-N-R_2$-pyrrolidinium, wherein R_1 and
R_2 are alkyl groups and wherein R_3-R_{10} are either: H; F;
separate alkyl groups which may be branched, substituted
and comprise heteroatoms; separate phenyl groups which
may be substituted and comprise heteroatoms. In the
electrochemical element according to the invention is it
preferred that R_1 is methyl and R_2 is butyl or hexyl or
that $R_1=R_2$ is butyl.

FIG. 1B depicts the chemical structure of 1-butyl-1-
methyl-pyrrolidinium and FIG.1C depicts the chemical
structure of 1-butyl-2,2,3,3,4,4,5,5-octafluoro-1-methyl-
pyrrolidinium.

Several rechargeable batteries with electrolytes
comprising pyrrolidinium based ionic liquids were made
and tested using the manufacturing and testing procedures
that are described hereinbelow. Electrolytes were
synthesised by mixing pyrrolidinium based ionic liquids
and lithium salts. The following acronyms will be used:

P_{14}=1-methyl-1-butyl-pyrrolidinium

P_{16}=1-methyl-1-hexyl-pyrrolidinium

P_{44}=di-butyl-pyrrolidinium

TFSI=bis(trifluoromethylsulfonyl)imide=$N(CF_3SO_2)_2^-$

P_{14}TFSI and P_{16}TFSI (acquired from Merck KGaA) were dried under dynamic vacuum at 90 °C for 48 hours. The salts LiTFSI (LiN$(CF_3SO_2)_2$, 3M) and Lithium-perchlorate (LiClO$_4$, from Alfa Aesar) were dried under dynamic vacuum at 130 °C for 48 hour. After being dried, the materials were transferred into a helium filled glovebox (water content <5 ppm). The following electrolytes were made by mixing the appropriate amounts of ionic liquid and salt, resulting in clear and stable liquids:

5 mol% LiTFSI in P_{14}TFSI

0.38 mol LiTFSI in 0.62 mol P_{14}TFSI

0.40 mol LiTFSI in 0.60 mol P_{14}TFSI

2.0 mol/kg LiTFSI in P_{16}TFSI

1.0 mol/kg LiClO$_4$ in P_{14}TFSI

0.30 mol LiTFSI in 0.70 mol P_{44}TFSI

Electrodes were made of LiCrTiO$_4$, Li$_4$Ti$_5$O$_{12}$, LiFePO$_4$ and TiS$_2$ and were coated as follows.

The electrodes were made by the doctor-blade technique on Aluminium or Copper foil current collectors using a paste of the active materials. The pastes contained typically 80 w% active material, 10-13 w% conductive additives, and 7-10 w% of a binder dissolved in 1-methyl-2-pyrrolidon (Merck KGaA). The conductive additives were a mixture of carbon black (2-10%, SuperP from MMM) and graphite (0-10 w%, KS4 from Timcal). The binder was either polyvinylidenefluoride (PVDF, from Solvay) or polymethylmethacrylate (PMMA). LiCrTiO$_4$ and LiFePO$_4$ were synthesised in house, Li$_4$Ti$_5$O$_{12}$ was obtained

from Hohsen Corporation Japan, TiS_2 was obtained from Alfa Aesar, $LiMn_2O_4$ was obtained from Sedema. The coatings were dried at 140 °C for about 15 minutes, densified using a Durston rolling mill, and further dried overnight under dynamic vacuum at 80 °C. Finally, samples of 15 mm diameter, with a typical capacity of 1-2 mAh, were punched out and used for testing.

All measurement were done using CR2320 type coincells (23 mm diameter, 2 mm high, 304 steel, acquired from Hohsen Corporation Japan), with polypropylene (PP) or polytetrafluoroethylene (PTFE) gaskets, or in 304 steel cells with high temperature viton O-rings. All cells were assembled in a glovebox. Typically, a cell was made by stacking in a can: an electrode, a 21 mm diameter glassfiber mat (type GF/C, Whatman), a gasket, 4-5 drops of electrolyte with a 1 ml polyethylene pipet, a 17 mm diameter Lithium disk 0.38 mm thick (Chemetall), a 17 mm diameter pressing plate 0.2 mm thick, a 15 mm diameter wave-spring, and a cap which was insulated by tape. If necessary, the electrolyte was warmed to about 100 °C to reduce the viscosity. The cells were closed in a manual CR2320 crimping tool (Hohsen Corporation Japan).

Testing of batteries

The cells were cycled (subsequent charging and discharging) in air in climate chambers (±0.1 °C accuracy) using Maccor S4000 battery testers. The cells were subjected to various current densities, ranging from 0.1 to 1.0 C-rate. Within a cycle the current was constant and equal for discharging and charging. The 1 C-rate is here defined as the current needed to fully discharge the battery in 1 hour as calculated from the mass of active material and its specific storage

capacity. Thus, ideally a 0.1C-rate discharge lasts for 10 hours and a 2.0 C-rate lasts 0.5 hour.

EXAMPLE I:

"Testing at 110° of a rechargeable battery with a $Li_4Ti_5O_{12}$ cathode, a Lithium metal anode and an electrolyte comprising LiTFSI in $P_{14}TFSI$"

A coincell was made according to the procedures described above. $Li_4Ti_5O_{12}$ was used as the cathode material with PvdF as binder on an Aluminium current collector. The electrolyte was a mixture of LiTFSI dissolved in $P_{14}TFSI$ in the molar ratio of 0.38:0.62. The cell was cycled 242 times between 1.0 and 2.0 V at 110 °C.

In the first 29 cycles the current was varied between 0.1 and 1.0 °C. FIG. 2 shows the capacity for discharging and charging as percentage of the expected sample capacity. Very stable cycling behaviour of the battery was found with good rate capability and high efficiency. The voltage curves in FIG. 3 show the typical voltage curve of $Li_4Ti_5O_{12}$ versus lithium for the 7-th, 107-th and 207-th cycle for the same current density indicating that the active material did not change and did not loose its integrity.

EXAMPLE II:

"Testing at 110 °C of a rechargeable battery with a $Li_4Ti_5O_{12}$ cathode, a Lithium metal anode and an electrolyte comprising LiTFSI in $P_{16}TFSI$"

A coincell was made according to the procedures described above. $Li_4Ti_5O_{12}$ was used as the cathode material with PvdF as binder on an Aluminium current collector. The electrolyte was a 2.0 mol/kg mixture of

LiTFSI dissolved in $P_{16}TFSI$. The cell was cycled
150 times between 1.0 and 2.0 V at 110 °C.

    In the first 29 cycles the current was varied between
0.1 and 1.0 °C. FIG. 4 shows the capacity for discharging
and charging as percentage of the expected sample
capacity. Very stable cycling behaviour of the battery
was found with good rate capability and high efficiency.

EXAMPLE III:

"Testing at 110 °C of a rechargeable battery with a TiS_2
cathode, a Lithium metal anode and an electrolyte
comprising LiTFSI in $P_{14}TFSI$"

    A coincell was made according to the procedures
described above. TiS_2 was used as the cathode material
with PvdF as binder on an Aluminium current collector.
The electrolyte was a mixture of LiTFSI dissolved in
$P_{14}TFSI$ in the molar ratio of 0.40:0.60. The cell was
cycled 13 times between 1.8 and 2.5 V and 87 times
between 1.5 and 2.5 V at 110 °C.

    FIG. 5 shows the capacity for discharging and
charging as percentage of the expected sample capacity.
The lowering of the lower cut-off voltage increased the
capacity substantially. Apart from some initial fading
the cycling is fairly stable and with high efficiency.
The voltage curves in FIG. 6 shows the typical voltage
curve of TiS_2 versus lithium for the 50-th cycle.

EXAMPLE IV:

"Testing at 150 °C of a rechargeable battery with a
$Li_4Ti_5O_{12}$ cathode, a Lithium metal anode and an
electrolyte comprising LiTFSI in $P_{44}TFSI$"

    A coincell was made according to the procedures
described above. $Li_4Ti_5O_{12}$ was used as the cathode
material with PvdF as binder on an Aluminium current

collector. The electrolyte was a mixture of LiTFSI dissolved in $P_{44}TFSI$ (di-butyl-pyrrolidinium-TFSI) in the molar ratio 0.30:0.70. The cell was cycled 60 times between 1.0 and 2.0 V at 150 °C. The current was varied between a 0.1, 0.5, and 1.0C-rate.

FIG. 7 shows the capacity for discharging and charging as percentage of the expected sample capacity. Even at 150 °C the cycling stability is very good and similar to that at 110 °C demonstrating the use of these electroloytes in high temperature batteries.

EXAMPLE V:

"Testing at 110 °C of a rechargeable battery with a 4.1 V $LiMn_2O_4$ cathode, a Lithium metal anode and an electrolyte comprising LiTFSI in $P_{14}TFSI$ or $P_{16}TFSI$"

Three coincells were made according to the procedures described above. $LiMn_2O_4$ was used as the cathode material with PvdF as binder on a 304-steel current collector. The electrolytes were:

A. 1 M $LiPF_6$ in EC/DMC 2:1 w/w;

B. 0.05 mol LiTFSI dissolved in 0.95 mol $P_{14}TFSI$

C. 1 mol/kg LiTFSI dissolved in $P_{16}TFSI$

The cells were charged and discharged between 3.5 and 4.3 V at 25 °C for electrolyte A and at 110 °C for electrolyte B and C. The current was a 0.1C-rate.

FIG. 8 shows the potential curves for the three cells. The reference cell with electrolyte A shows the expected characteristic potential curve for $LiMn_2O_4$ being symmetrical in charge and discharge. The cell with electrolyte B did not reach a potential higher than 4 V and failed. The cell with electrolyte C showed a too small charge capacity and an even smaller discharge

capacity. The specific $LiMn_2O_4$ potential curve is lost
and the capacity faded quickly. These tests demonstrate
that the pyrrolidinium based electrolytes cannot be used
with intercalation materials which have an upper

5   reversible-potential-limit higher than 4 V versus Li/Li^+.
EXAMPLE VI:
"Testing at 110 °C of a rechargeable battery with a 3.4 V
$LiFePO_4$ cathode, a Lithium metal anode and an electrolyte
comprising LiTFSI in $P_{14}TFSI$"

10   A coincell was made according to the procedures
described above. $LiFePO_4$ was used as the cathode material
with PvdF as binder on an Aluminium current collector.
The electrolyte was a mixture of LiTFSI dissolved in
$P_{14}TFSI$ in the molar ratio 0.40:0.60. The cell was cycled

15   between 3.0 and 3.8 V as the upper cut-off potential at
110 °C. The current was a 0.1C-rate.
FIG. 9 shows the characteristic flat potential curve
for $LiFePO_4$, being symmetrical for charge and discharge.
This tests demonstrates that the pyrrolidinium based

20   electrolytes can be used with intercalation materials
with an upper reversible-potential-limit up to 4 V versus
Li/Li^+.
EXAMPLES I-VI and FIG. 1-9 demonstrate that the
tested cells with pyrrolidinium based ionic liquid

25   electrolytes and with a cathode comprising an
intercalation material having an upper reversible-
potential-limit (RPL_{upp}) of at most 4 V versus Li/Li^+ are
suitable for use as rechargeable batteries at a high
temperature of up to at least 150 °C.

30   The examples further indicate that suitable materials
for use in the rechargeable batteries are:

- $Li_4Ti_5O_{12}$, $Li_4Mn_5O_{12}$, $LiCrTiO_4$, and TiS_2 as active intercalation materials.

It is also believed that other known intercalation materials as for example $Li_{1+y}Mn_{2-y}O_4$ (~2.9 V insertion, $0 \leq y \leq 1/3$), $LiMg_yNi_{0.5-y}Mn_{1.5}O_4$ (~2.9 V insertion, $0 \leq y \leq 0.5$), $Li_2Mn_4O_9$ (~2.9 V insertion), Li_7MnN_4, and Li_3FeN_2 can be used.

- Aluminium and stainless steel SUS304 as a current collector materials.

It is also believed that other materials as for example Nickel, Copper, Gold, Platinum, Carbon, and Graphite can be used as current collectors.

- PvdF and PMMA as binder materials.

It is also believed that other known binder materials as for example PTFE, PCTFE, ECTFE, ETFE, and FEP can be suitable binder materials.

- Carbon black and graphite as conductive additives.

It is also believed that instead or together with Carbon black and Graphite it is possible to use a metal foam or similar porous but electronically conductive structure, glassy carbon, or a metal powder as a conductive matrix in the electrodes. This can be an advantage in case Carbon black and/or graphite cause unwanted side reactions with other materials in the battery.

- porous glassfiber mat as separator material.

It is also believed that for example porous layers comprising Al_2O_3, MgO, Li-β-Alumina are suitable separator materials.

Mixtures of $P_{14}TFSI$, $P_{16}TFSI$ and $P_{44}TFSI$ with LiTFSI and/or $LiClO_4$.